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Morphology and Crystal Structure of Wholly Aromatic All-Para Polyamide-Hydrazide Polymers

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ABSTRACT

The morphology of some amide-hydrazide polymers of the type useful for high-modulus X-500 class fibers has been characterized by transmission electron microscopy of thin films crystallized from dilute solution. Selected area electron diffraction was used to characterize the crystallinity and crystal structure of the thin films and precipitated polymer. The films were cast from concentrated solutions and crystallized by heating the films. The results of these studies revealed several unique features relative to the crystal structure of the all-para polymers. Thin films of the crystallized polymer showed a distinctive crystalline texture—the molecular chains were found to be preferentially oriented parallel to the film plane and randomly oriented about an axis normal to the film plane. Electron diffraction measurements showed equatorial reflection

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maxima at tilt angles of ±30, ±48, and ±59 when the films were tilted on an axis parallel to the film plane. From these results a tentative crystal unit cell and theoretical crystal density were determined: a = 8.5 Å, b = 4.9 Å, c (chain axis) = 29.6 Å, ρ (density) = 1.51 g/cc. The value a/b = 1.735, which is very near $3^{1/2}$, implies essentially hexagonal packing of the chains. Crystallization from dilute solution revealed lamellar structures resembling "single crystals" in the electron microscope similar to those observed in other crystalline polymers. However, in contrast to these other polymers, these "crystals" are not likely to contain folded chains because of the very rigid nature of the all-para polyamide-hydrazide.

It has been pointed out by W. B. Black [1] that fibers made from wholly aromatic, all-para polyamide-hydrazide polymers of Monsanto's X-500 class of polymers show extremely high experimental moduli relative to the theoretically predicted moduli for this polymer type (up to 65% of theoretical). This fact implies a highly ordered arrangement of the molecular chains.

From structural considerations, the all-para polymers are likely composed of very rigid, inflexible molecules. In support of this "extended-chain" nature, Miller [2], using x-ray diffraction techniques, reported a "collagen-like" appearance of the fiber pattern, i.e., many sharp peaks on the meridian and only rather diffuse scattering on the equator. In order to characterize the morphology and crystal structure of some of these aromatic, all-para polyamide-hydrazide polymers, transmission electron microscope and electron diffraction techniques were used. Two methods of sample preparation were used:

(a) Casting of thin films from concentrated "dopes."
(b) Precipitation of crystalline structures from dilute solution.

In method (a), thin films were prepared by smearing a drop of the concentrated polymer solution on a glass slide and allowing the solvent to evaporate. The films were then subjected to various treatments, such as heating in the presence of nitrogen (up to 350°C) and stretching. The films were cut into small pieces and examined in the transmission electron microscope. In some instances the films were heated in the electron microscope itself by using a special heating stage.

In method (b), crystallinization from dilute solution was accomplished by heating a 1% solution of the polymer (using either dimethyl acetamide or dimethyl sulfoxide as solvent) to 60°C for a few minutes, then cooling to room temperature. A drop of the suspension was placed on a carbon-coated grid. After the solvent was evaporated, the samples were shadowed with platinum and examined in the transmission electron microscope. The metal evaporation step was omitted for electron diffraction experiments. A Philips EM 200 electron microscope was used in this study.

RESULTS

Thin Films

Figure 1 shows the electron diffraction pattern of an "as-cast" film. Only two diffuse rings—one at about 4 Å and the other at 2 Å—are visible in the pattern. After heating the films at about 350°C for a few minutes the pattern shown in Fig. 2 was obtained. Many more reflections than are shown here can be measured from the negative. Figure 3 is a drawing which depicts a typical diffraction pattern showing nine discrete reflections from an annealed film.

On drawing an annealed film, a pattern such as shown in Fig. 4 is obtained. Note the position of the three strong reflections at 7.4, 4.3, and 2.1 Å. Also note the similarity between this pattern and the one shown in Fig. 5, which results from tilting an annealed, unoriented film through an angle of 30°. (The untilted film has a ring pattern similar to that shown in Fig. 2.)

From these results, it is reasonable to deduce the following:

(a) The 7.4 and 2.1 Å reflections arise from crystalline planes which are normal to the molecular chains, i.e., (001) reflections.

(b) The 4.3 Å reflection, being normal to the 7.4 and 2.1 Å reflection orientation, arises from planes which are parallel to the molecular chains, i.e., (hk0) reflections.

(c) In an unoriented film, the crystallites are arranged such that the molecular chains lie in the film plane, randomly oriented about an axis normal to the film plane.

Crystallites in a thin film frequently exhibit a texture or a preferred arrangement due partly to the space constrictions placed upon the crystallites and partly to the morphology of the

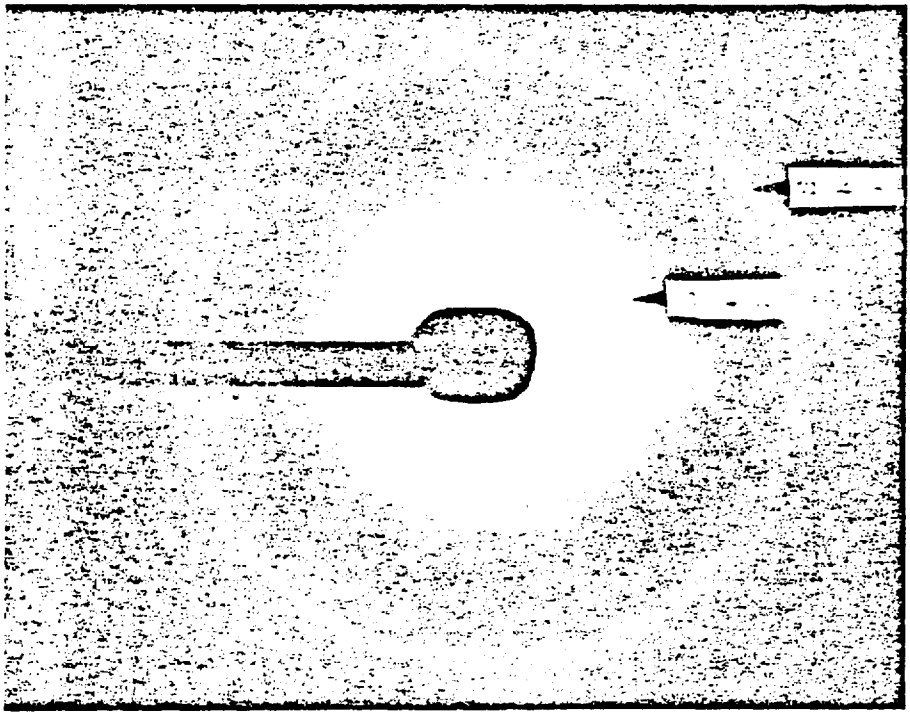

FIG. 1. Electron diffraction pattern of "as-cast" polyamide-hydrazide film.

crystallizing units. The texture can be detected if, when a film is tilted about an axis in the film plane, certain reflections show their maxima at discrete tilt angles. If there were no texture present, the diffraction pattern would not change as a result of tilting, i.e., one would obtain random, ring patterns at all tilt angles. In the present case a distinct texture was evident in the diffraction patterns of the thin films. In fact, by identifying the reflection maxima as a function of tilt angle, it is possible to ascribe a tentative unit cell to the crystal. Three reflections, 4.3, 3.2, and 2.5 Å, had their maxima on the equatorial position on tilting a film at angles of 30, 48, and 59°, respectively. When these results are plotted, using the reciprocal of the spacings as the vectors at the appropriate angle, a cell with a = 8.5 Å and b = 4.9 Å is derived (Fig. 6).

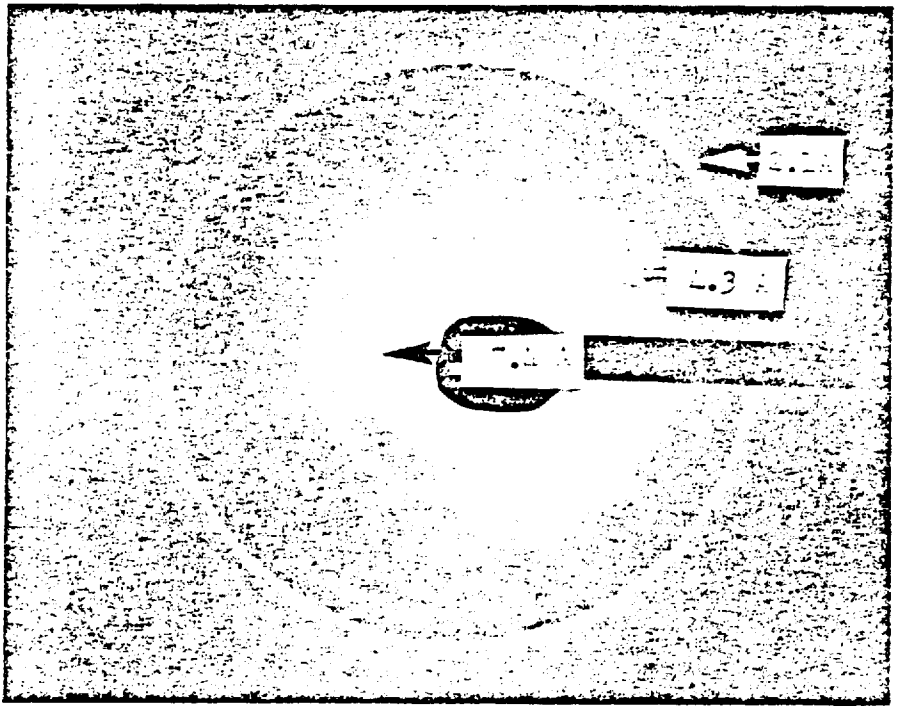

FIG. 2. Electron diffraction pattern of polyamide-hydrazide film heated to 350°C.

The c axis repeat (along chain axes) is related to the 7.4 and 2.1 Å spacings previously noted. From x-ray results of R. L. Miller, on drawn fibers [2], several other reflections have been identified as arising from a repeat along the molecular chain. These are at 5.0, 3.7, 3.0, and 2.5 Å. All of these reflections can be accounted for by assuming an essentially extended chain with a repeat of ~29.6 Å for each molecular unit of the polymer [2]. Thus, according to Miller, 7.4 Å is the (004) reflection, 5.0 Å is (006), 3.7 Å is (008), 3.0 Å is (0010), 2.5 Å is (0012), and 2.1 Å is (0014).

The complete tentative unit cell is therefore given by the parameters a = 8.5 Å, b = 4.9 Å, and c = 29.6 Å. The ratio a/b is 1.735, which is very near $3^{1/2}$, implying a unit cell close to hexagonal symmetry (possibly orthorhombic or monoclinic).

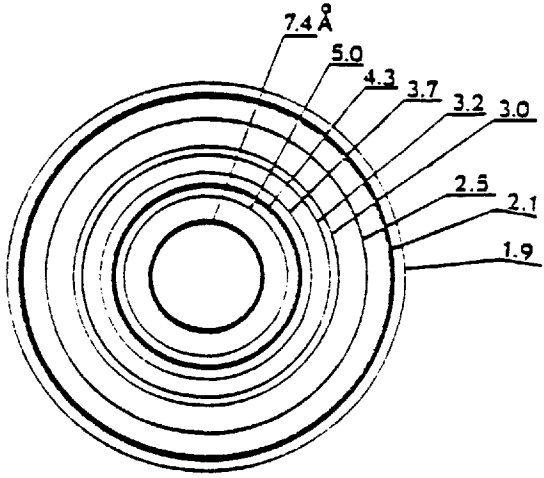

FIG. 3. Drawing taken from electron diffraction pattern of heated polyamide-hydrazide film showing 9 reflections.

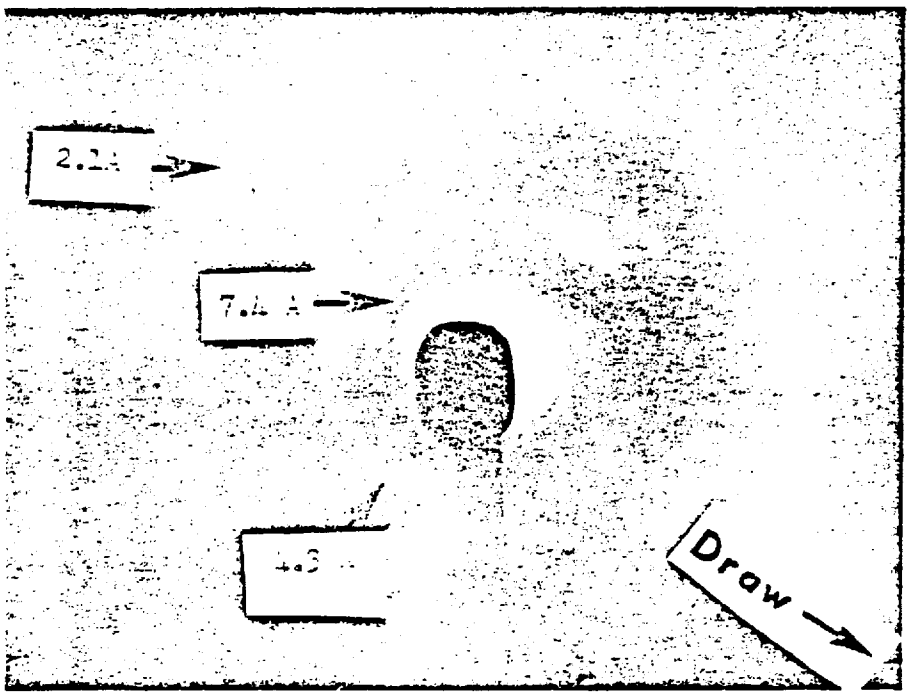

FIG. 4. Electron diffraction pattern of drawn, heated (350°C) film of polyamide-hydrazide polymer.

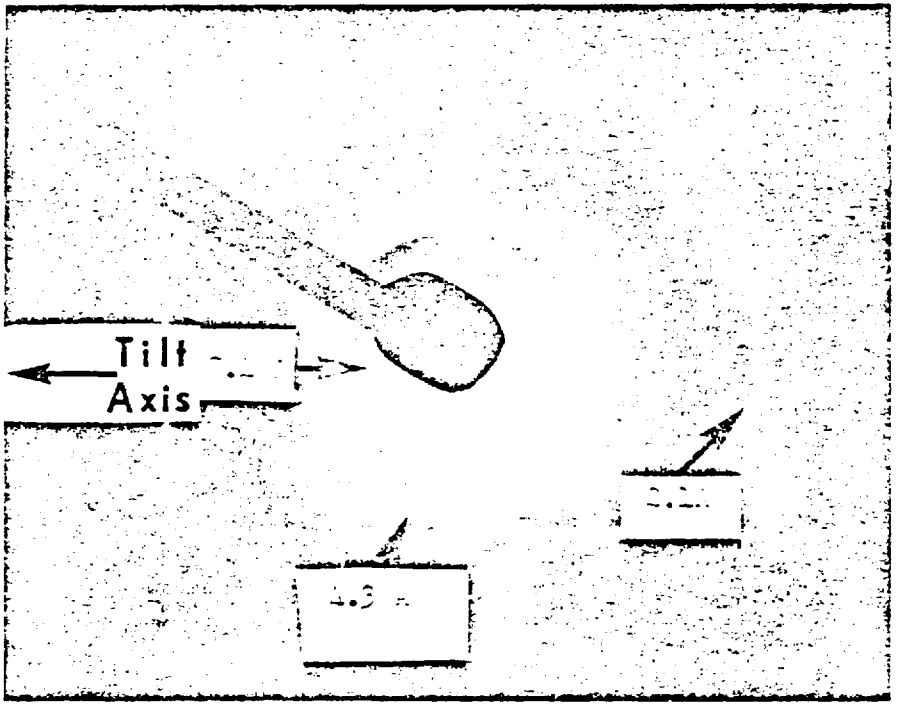

FIG. 5. Electron diffraction pattern of undrawn, heated (350°C) film of polyamide-hydrazide polymer. Film tilted 30°.

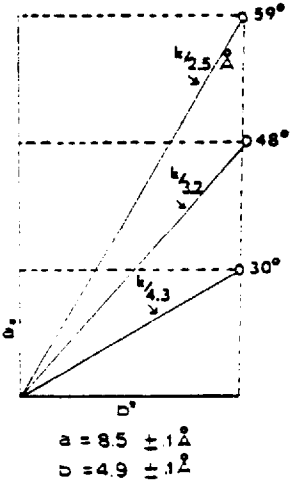

FIG. 6. Tentative unit cell calculation based on (hk0) reflection maxima at three tilt angles.

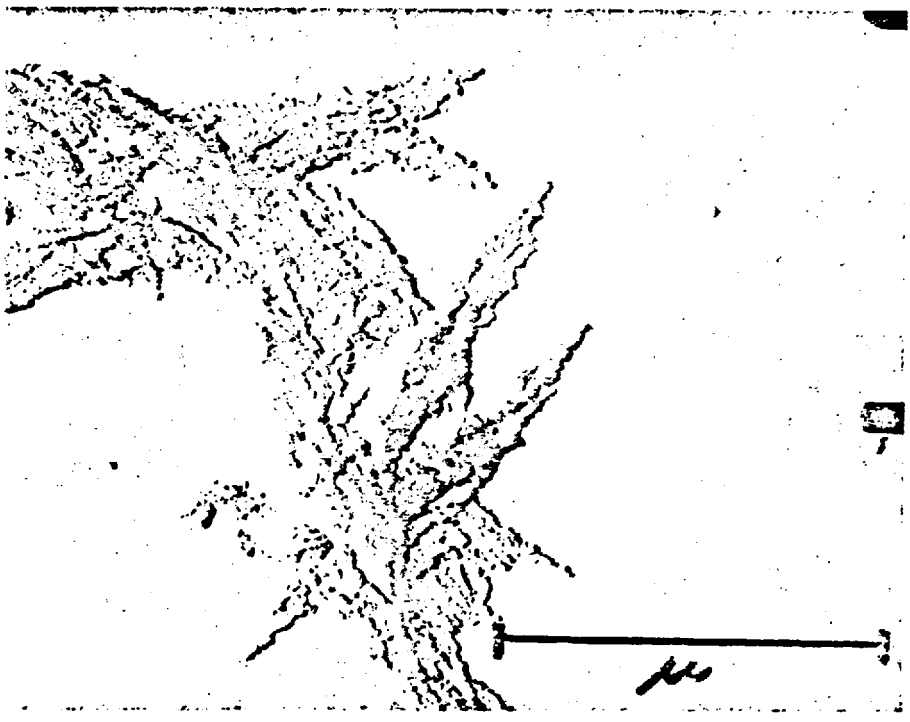

FIG. 7. Electron micrograph of irregular crystal lamellae precipitated from polyamide-hydrazide dilute solution (47,000× on original).

If we assume two molecules per unit cell, a theoretical density of 1.51 g/cc is obtained. The highest experimental density of this particular polymer is somewhat less than 1.51 g/cc.

Precipitation from Dilute Solution

Precipitation of an aromatic all-para amide-hydrazide polymer from dilute solution resulted in the structures shown in Figs. 7 and 8. Lamellar-like crystals were obtained resembling those observed in other crystalline polymers—in particular, polyacrylonitrile [3]. The lamellae are in the range of 100-150 Å in thickness. Electron diffraction of these crystals (Fig. 9) showed only two reflections, at 4.3 and 3.2 Å, corresponding to the {(200), (110)} and (210) planes, respectively. None of the reflections associated with a repeat along the chain axis were found, which implies

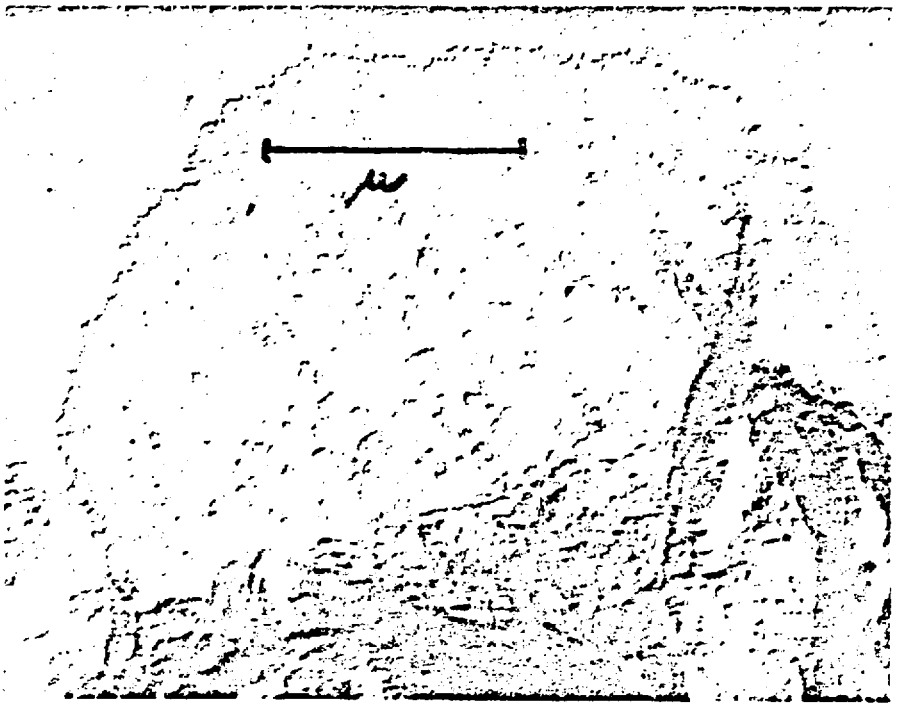

FIG. 8. Electron micrograph of large lamella precipitated from polyamide-hydrazide dilute solution (32,000× on original).

that the molecular chains do not lie in the plane of the lamellae. The chains are therefore most likely normal (or nearly normal) to the lamellae surfaces. For long-chain polymers of reasonably high molecular weight, this type of chain orientation usually means that the chains must fold in order to be accommodated within the thin lamellae. However, in the present case, it is believed that the molecular chains of this aromatic polymer are too rigid to fold (at least to fold as sharply as polyethylene chains). In support of this proposal, no evidence for the presence of microfibrils between fracture faces was found when the lamellae were fractured in tension. Such microfibrils are usually observed in the fracture of crystalline lamellae grown from solutions of high molecular weight, flexible polymers. Therefore, it is proposed that these lamellar structures result from the crystallization of a paraffin-like, low molecular weight fraction in the polymer solution.

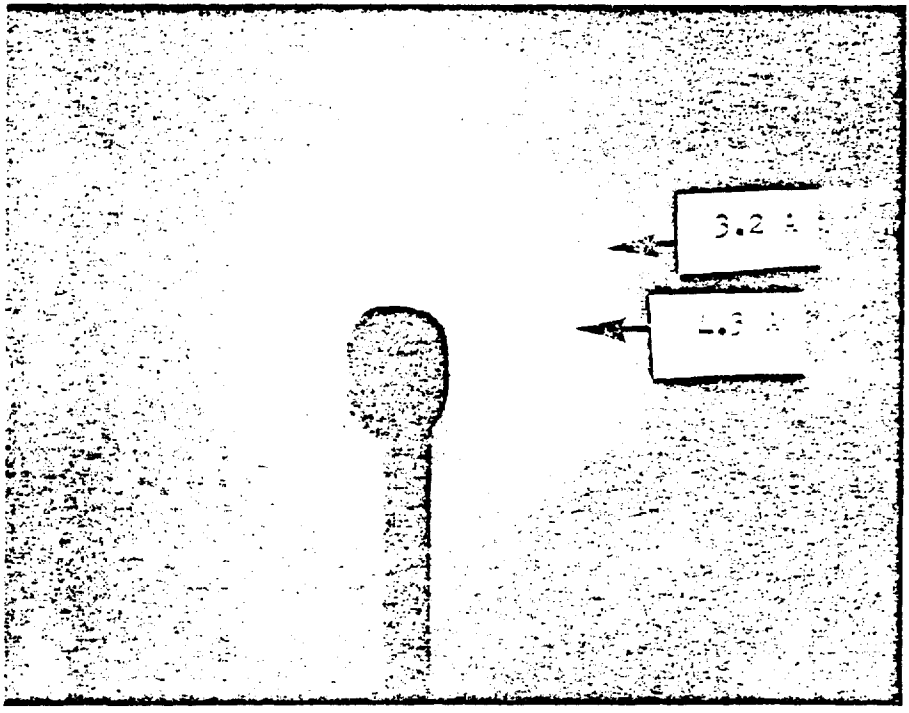

FIG. 9. Electron diffraction pattern from several lamellae precipitated from polyamide-hydrazide dilute solution.

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